

Solution-Processed Inorganic Solar Cell Based on in Situ Synthesis and Film Deposition of CuInS₂ Nanocrystals

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Solution-processed photovoltaic devices offer a route for harvesting solar energy that is appealing because of simplified and low-cost device fabrication, large-area coverage, and the possibility of producing mechanically flexible devices. Conjugated polymers have been widely investigated for this purpose and have achieved 6.1% solar power conversion efficiency.¹ Recently, new photovoltaics based on solution-processed inorganic nanocrystals (NCs) have attracted considerable attention, and photovoltaic devices based on systems such as CdTe,² CdSe,³ Cu₂S,⁴ PbS,^{5,6} Pb(S_xSe_{1-x}),^{7,8} CuInSe₂, CuInS₂,^{9,10} CuInGaS₄Se_{1-x},¹¹ and Cu₂ZnSnS₄^{12,13} have been demonstrated. Despite their appealing advantages over conjugated polymer technologies, (e.g., a significantly larger carrier mobility), many of the approaches utilizing NCs suffer from the need to synthesize the NC capped with long-chain ligands that act as an insulator in photovoltaic devices, or include an additional ligand-exchange processing step to shorter and more volatile ligands.²⁻⁸ Here we present a simple route for the fabrication of optoelectronic devices that involves film deposition with in situ synthesis, thereby circumventing the need to first synthesize the NCs and then perform a ligand exchange. We demonstrate the utility of this approach for the fabrication of both the absorber and buffer layers of CuInS₂ (CIS) solar cells.

Our method of using a molecular-based precursor solution is similar to the one used with hydrazine,¹⁴ but it utilizes significantly less toxic solvents and also enables the deposition of both the solar-cell absorber and buffer layers. We use 1-butylamine and 1-propionic acid, which act as solvents and reaction stabilizers. Typically, after the precursors needed for the film formation are dissolved, the precursor solution is spin-cast or drop-cast directly onto a substrate and dried at moderate temperature before being heated to a higher temperature that accelerates the reaction of the precursor and film formation. Successive film depositions of the CIS absorber layer on an indium tin oxide (ITO)-coated glass substrate, the CdS buffer layer, and an Al electrode produced a solar cell with a power conversion efficiency of 4%. We believe that with device optimization a much greater power conversion efficiency is attainable.

A typical synthesis of a CIS NC film proceeded as follows: In(OAc)₃ (0.1 mmol), CuI (0.11 mmol), and thiourea (0.5 mmol) were mixed with 0.6 mL of 1-butylamine and 40 μL of 1-propionic acid under an inert atmosphere in a glovebox. The mixture was shaken for 1 min, after which the precursors had dissolved and the color of the reaction solution had begun to change from colorless to light-yellow. The substrates used were commercial ITO-coated glass plates that were cleaned prior to film deposition by ultrasonication for 30 min in acetone and then 2-propanol. Under an inert atmosphere in a glovebox, the CIS precursor solution was spin-cast onto the substrates at 1300 rpm for 30 s. The films were then placed on a 150 °C hot plate for 10 min in order to eliminate the volatile solvent and then heated to 250 °C at a rate of 10 °C/min and kept an additional 10 min at this temperature in order to induce sintering. The CdS precursor solution was prepared in a similar

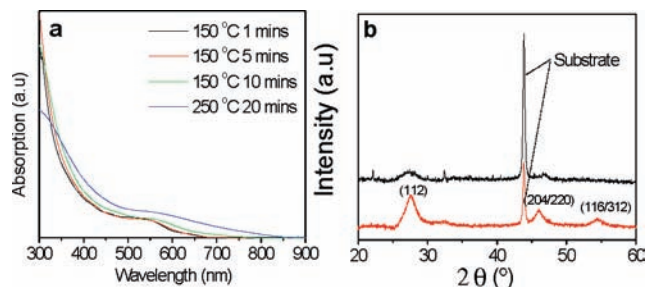


Figure 1. (a) UV-vis absorption spectra indicating the growth of CIS nanocrystals for various film-heating durations. (b) XRD pattern of a film annealed at 150 °C for 5 min (upper pattern) and a film first heated at 150 °C for 10 min and then heated to 250 °C within 10 min and kept for an additional 10 min at this temperature (lower pattern).

way as the CIS: CdCl₂ (0.1 mmol) and thiourea (0.3 mmol) were mixed with 1 mL of 1-butylamine and 40 μL of 1-propionic acid. The CdS precursor solution was spin-cast directly onto the CIS layer at 2000 rpm for 60s, and then the device was heated on a hot plate at 250 °C for 10 min. A second CdS layer was deposited under the same conditions, after which the device was heated for 5 min. An 80 nm thick thermally evaporated Al top electrode deposited at a pressure of 10⁻⁶ Torr completed the device fabrication. The active area of the device was 4.5 mm². Current-voltage (*I*-*V*) measurements were performed using a Keithley 236 sourcemeter, and the devices were illuminated with a NIST-calibrated AM 1.5G Oriel solar simulator that had an intensity of 100 mW/cm².

During the heating treatment, the film that was forming changed from colorless to yellow to red and finally stabilized as a semitransparent shiny black. This color evolution is similar to the one we observed previously in the synthesis of CIS NCs in solution.¹⁵ The absorption spectra of the CIS film taken at different heating durations were measured with a UV-vis absorbance spectrometer and are shown in Figure 1a. The onset of the absorption spectra underwent a red shift with increasing annealing time, indicating the growth of the CIS NCs. The observed shoulder may have originated from excitonic absorption of the NCs. Figure 1b shows the powder X-ray diffraction (XRD) pattern of the as-synthesized CIS samples after they were heated at different temperatures and time durations. The XRD data indicate a polycrystalline structure and narrower diffraction peaks for the film annealed at a higher temperature.

Scanning electron microscopy (SEM) top and cross-sectional images of a CIS/CdS NC film during various stages of fabrication are displayed in Figure 2. As Figure 2a shows, the CIS particles appear to be touching or even fused together, a film morphology that facilitates enhanced carrier transport. Heating the CIS film at 250 °C seemed to produce a structure that has some voids, possibly resulting from decomposition of volatile surface ligands and precursor materials. During the spin-coating of the CdS layer, these

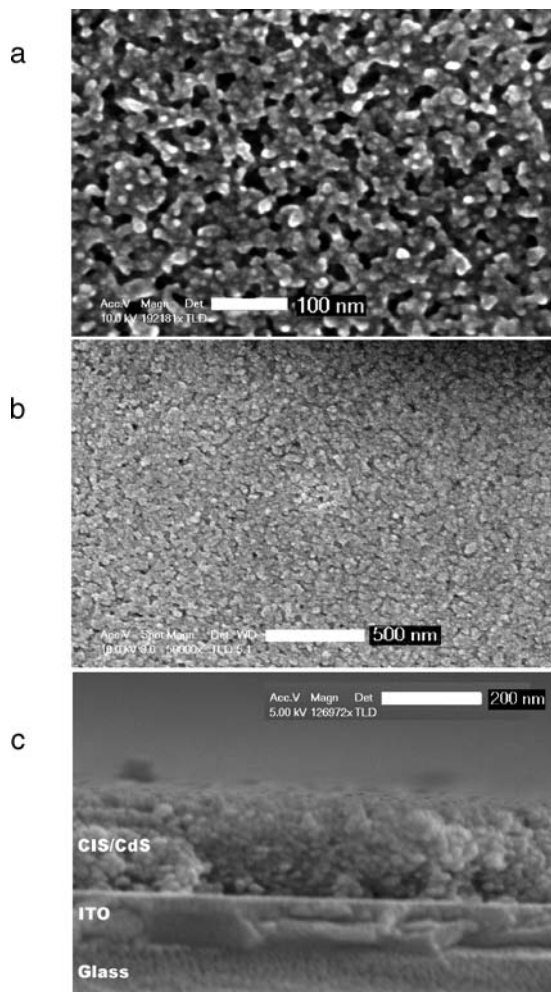


Figure 2. SEM images of a CIS film. (a) Typical top-view SEM image of the CIS film after heat treatment at 250 °C. (b) Top-view SEM images of the CIS film after CdS deposition. (c) Cross-sectional view of the active layer on ITO glass; the bottom two layers are glass and ITO, while the top layer is the CIS/CdS film.

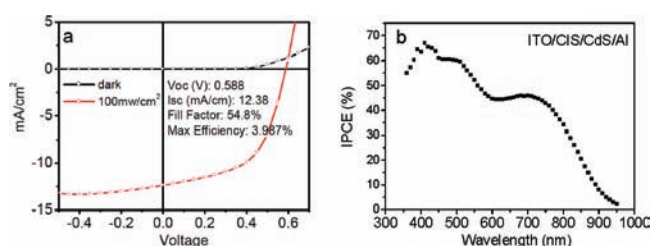


Figure 3. (a) I – V characteristics and (b) IPCE spectrum of the ITO/CIS/CdS/Al solar cell.

voids could have been filled by the CdS precursor solution and thereby formed an interpenetrating heterojunction structure at the absorber–buffer interface.

The I – V characteristics of a typical solar cell fabricated using the in situ approach are shown in Figure 3a, and the incident photon conversion efficiency (IPCE) spectrum is shown in Figure 3b. The CIS/CdS device exhibits an efficiency of 4% for illumination with a solar simulator having an intensity of 100 mW/cm² that was calibrated with a c-Si reference solar cell. Device characteristics

are as follows: $V_{oc} = 0.588$ V, $J_{sc} = 12.38$ mA/cm², and $FF = 54.8\%$. The V_{oc} and J_{sc} of this device are on the order of those obtained using other non-vacuum-based techniques.^{9,13}

The present synthetic route is distinct, as it incorporates organic ligands that facilitate formation of quantum dots. The heat treatment initiates the quantum dot growth and sintering while the dots are rather small, thereby enabling sintering at relatively low temperatures.

We note that the data presented were taken from devices with a simplified architecture and that optimizing the device fabrication as well as adopting an architecture that incorporates a Mo electrode as well as ZnO and antireflection layers can lead to higher power conversion efficiency.

In summary, a novel, reproducible, and simple solution-based process for the fabrication of the CIS absorber layer and CdS buffer layers, involving deposition of a precursor solution on a substrate followed by in situ formation of NCs at temperatures as low as 250 °C, has been presented; the photovoltaic device fabricated using this process exhibits an efficiency of 4%. This fabrication approach eliminates the need for processing steps such as chemical-bath deposition of the CdS layer, high-temperature post-deposition sulfurization treatment, and a cyanide-bath etch step to correct phase purity and grain size. The initial results demonstrate the promise of this alternative approach for the fabrication of thin-film CIS/CdS solar cells. This synthetic route is robust, low-cost, and environmentally friendly and could be applicable to many semiconductor systems for fabrication of high quality electro-optic devices.

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